

PROCESS FOR THE PREPARATION OF THERMALLY STABLE POLYOXYMETHYLENE COPOLYMERS

Process for the preparation of thermally stable polyoxymethylene copolymers

The present invention relates to a process for the preparation of thermally stable polyoxymethylene (POM) copolymers wherein the initiator is distributed within the monomers through prior dissolution in a formaldehyde dialkylacetal.

Thermoplastic molding materials of POM homopolymers and copolymers have long been frequently used as versatile materials of construction, particularly in engineering and manufacturing. In many cases they can be used as a substitute for metals on account of their outstanding mechanical properties, such as high rigidity, hardness and strength and the fact that it is possible to produce moldings and molded parts to strict tolerance limits, and their good resistance to many chemicals.

It is known that, by copolymerizing trioxane with cyclic ethers or cyclic acetals, copolymers can be obtained in which the sequence of the $-\text{CH}_2-\text{O}-$ groups is interrupted by randomly distributed comonomer units such as $-\text{CH}_2\text{CH}_2-\text{O}-$, $-(\text{CH}_2)_4-\text{O}-$ or $-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$ (G. W. Becker/D. Braun, *Kunststoff-Handbuch*, Vol. 3/1, p. 303, Munich-Vienna, 1992). The comonomers are normally used in a weight proportion of 0.2 to 20%. Suitable initiators used in the present invention are strong protonic acids selected from the group consisting of trifluoromethanesulfonic acid and anhydrides, pentafluoroethylsulfonic acid and anhydrides, heptafluoropropylsulfonic acid and anhydrides, nonafluorobutyl sulfonic acid and anhydrides, perfluoroheptylsulfonic acid and anhydrides, and mixtures thereof. Suitable initiators are also Lewis acids selected from the group consisting of phosphorus pentafluoride, silicon tetrafluoride, boron trifluoride, boron trifluoride etherates, tetrachloride, arsenic pentafluoride, triphenylmethyl hexafluorophosphate, and mixtures thereof.

At the end of the polymerization reaction the crude POM polymer still contains a certain amount of unconverted monomers and unstable terminals which have to be eliminated to stabilize the final product.

In order to be able to form such a polymer from the melt, as it is customary for thermoplastics, it is necessary to deactivate the polymerization initiator, to remove the adhering monomer residues from the polymer and to break down the unstable fractions.

Thus, it is known that the deactivation of the initiator is carried out in the aqueous phase or in an organic solvent, subsequent filtration, washing and drying steps being required. The deactivation of the initiator with the addition of different deactivators can also be effected in the melt (DE 3703790). The deactivation step is often carried out in combination with the demonomerization and the elimination of unstable chain ends (DE 37 38 632 and EP 0 137 305). EP 0673 955 describes a process in which crude polymer is treated with a steam which also contains small amounts of volatile base. In this way, unconverted residual monomer is removed and the initiator is deactivated. JP 05059255 states that the initiator is deactivated by adding alkali metal or alkaline earth metal oxides to the polymer melt.

The elimination of unstable terminal groups, which usually remain in the crude polymer after the polymerization and in particular lead to chain degradation when the polymer is heated, is also a usual process step in the preparation of POM copolymers. The unstable hemiacetal end groups in

trioxane copolymers can be selectively broken down, for example, by hydrolysis, i.e. by treating the copolymer at temperatures of from 120 to 220° C. with pressurized water comprising alkaline material, especially trialkylamines, and optionally with the addition of organic solvents, especially lower alcohols, trioxane or dioxolane (*Kunststoff Handbuch*, p. 316). After the hydrolysis, the polymer must be precipitated again, washed and dried.

The object of the invention therefore is to develop a process which makes it possible economically to prepare stable copolymers of 1,3,5-trioxane in a continuous process while avoiding the deficiencies of the known processes.

It has now been found that thermally stable POM polymers can be obtained if the initiator, which in general is a strong protonic acid, is first dissolved in a formaldehyde dialkylacetal, a substance which usually is known to regulate the molecular weight of the POM polymer, and then added to the reaction mixture. The invention eliminates the need to utilize an organic solvent carrier, an unnecessary component in the reaction mechanism, for the introduction of the protonic or Lewis acid into the reaction mixture.

The present invention accordingly relates to a process for preparing polyoxymethylene copolymers, wherein 1,3,5-trioxane is polymerized with generally known comonomers in the presence of a strong protonic acid initiator and in the presence of a formaldehyde dialkyl acetal, and wherein the initiator is dissolved in a portion of the formaldehyde dialkyl acetal before admixing the same with trioxane and the comonomers.

In the prior art process of the production of POM polymers, generally formaldehyde dialkyl acetals are used as molecular weight regulators. Generally, the use of a molecular weight regulator has not been known to produce high molecular weight polymers.

The advantage of the process according to the invention is, however, that through initial dissolution of the initiator in a formaldehyde dialkylacetal it is possible to add a very low quantity and controlled amount of the initiator in a perfectly dispersed state to the monomer mixture thereby controlling the reaction rate. Due to the very low quantity of initiator in the reaction mixture it is possible to also produce high molecular weight material although there is a small amount of molecular weight regulator present in the reaction mixture. According to the invention, it is possible to avoid contamination of the monomers and resulting polymer with substances which are critical to the polymerization process. For example, it is no longer necessary to add an agent to deactivate the initiator. In principle, it is also no longer necessary to perform hydrolysis to the crude polymer. However, to further reduce the content of unstable terminal groups in the polymer, it is advantageous to perform hydrolysis thereto.

In the process according to the invention, the initiator can be dissolved in a part of or in the total amount of formaldehyde dialkyl acetal used. The formaldehyde dialkyl acetal comprising the dissolved initiator usually is added to the mixture of trioxane and comonomers, i.e. the reaction mixture. A further predetermined amount of formaldehyde dialkyl acetal can be directly added to the reaction mixture before or after admixing the formaldehyde dialkyl acetal and dissolved initiator solution therewith.

In another working example, the formaldehyde dialkyl acetal containing the dissolved initiator is premixed with the comonomers before admixing the same with the trioxane. Optionally, a further predetermined amount of formaldehyde dialkyl acetal may be added to the reaction mixture afterwards.